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**GRAPHITE FIBER SURFACE ANALYSIS BY X-RAY
PHOTOELECTRON SPECTROSCOPY AND
POLAR/DISPERSIVE FREE ENERGY ANALYSIS**

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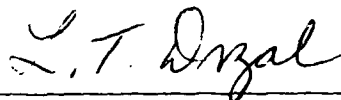
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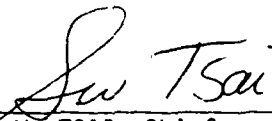
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spectroscopy (XPS) and contact angle measurements before and after a 300°C vacuum heat treatment. XPS spectra indicated multiple chemical states of carbon and oxygen and a reduction in the high energy binding state of carbon on the treated A fiber after vacuum heat treatment. Elemental surface concentrations have been calculated using corrected XPS peak areas. Contact angles were measured on these same fibers using a micro-Wilhelmy technique which incorporated eight liquids having a wide range of polar to dispersive free energy ratios. Determination of the fiber surface free energies and the proportions due to polar and dispersive components was made. Good correlation was found between the oxygen concentration as measured by XPS and the change in polar/dispersive ratios for the fibers with surface treatments.

FOREWORD

This technical report was prepared by L. T. Drzal of the Mechanics and Surface Interactions Branch, Materials Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson AFB, Ohio 45433 under Project 2419, "Nonmetallic and Composite Materials" and G. E. Hammer of Universal Energy Systems, Dayton, Ohio 45432, under contract F33615-77-C-5040, "Electron Spectroscopic Studies of Surfaces and Interfaces for Adhesively Bonded Surfaces".

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**GRAPHITE FIBER SURFACE ANALYSIS
BY X-RAY PHOTOELECTRON SPECTROSCOPY
AND POLAR/DISPERSIVE FREE ENERGY ANALYSIS**

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Graphite fibers of less than 10 μ in diameter are used as the reinforcing agents in structural epoxy matrix composite materials. Their efficiency in reinforcing is determined to a large degree by their degree of bonding to the epoxy. Commercial surface treatments maximize this adhesion without quantifying the interaction. The purpose of this work has been to relate the surface composition of commercial treated and untreated fibers to the "real" fiber surface incorporated in composites. Hercules A and HM fibers, treated and untreated, have been studied using X-ray photoelectron spectroscopy (XPS) and contact angle measurements before and after a 300 °C vacuum heat treatment. XPS spectra indicated multiple chemical states of carbon and oxygen and a reduction in the high energy binding state of carbon on the treated A fiber after vacuum heat treatment. Elemental surface concentrations have been calculated using corrected XPS peak areas. Contact angles were measured on these same fibers using a micro-Wilhelmy technique which incorporated eight liquids having a wide range of polar to dispersive free energy ratios. Determination of the fiber surface free energies and the proportions due to polar and dispersive components was made. Good correlation was found between the oxygen concentration as measured by XPS and the change in polar/dispersive ratios for the fibers with surface treatments.

1. Introduction

Advanced composite materials fabricated with graphite fibers and polymeric matrices are reliable, predictable materials used as structural components in aircraft. The ability of these composites to effectively use the strength and stiffness of their

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graphite reinforcing fibers depends on the properties of the matrix material and the degree of bonding between fiber and matrix. Many studies have attempted to correlate fiber surface properties to mechanical properties of composites but they have been for the most part unsuccessful in providing a basic understanding of the specific interactions that occur between fiber and matrix at the composite interface. X-ray photoelectron and Auger spectroscopic analysis of graphite fiber surfaces have been made and have noted the presence of surface oxygen on graphite fibers [1-3]. Measurements of this type, however, are made on well prepared samples in a vacuum environment. It is not known if the fiber surface species are added during surface treatment and if these species are able to interact with the composite matrix material after they have been exposed to the ambient environment.

Polar/dispersive surface free energy analysis determined through contact angle measurements has the potential for measuring the "effectiveness" of surface groups. This determination is done in the ambient air environment. Contact angles for a series of liquids of known polar and dispersive free energy content are measured gravimetrically on the fibers of interest. The fiber polar/dispersive free energy components are determined through analysis of the data according to the method proposed by Kaelble [4].

The purpose of this work is to determine the change in surface composition of various graphite fibers with treatment by XPS and to measure the corresponding changes in the polar/dispersive nature of the fiber surfaces through contact angle measurement.

2. Experimental

2.1. Graphite fibers

Two graphite fibers were chosen for this study. They were made from polyacrylonitrile based fibers using standard carbonization and graphitization techniques. One fiber was graphitized at approximately 1500°C and was designated as a type A fiber. The other was graphitized near 2600°C and was designated as a type HM fiber. The main structural elements of the graphite fibers are graphitic ribbons which lie roughly parallel to the fiber axis. These ribbons are formed of graphitic crystallites which increase in size with increasing graphitization temperature (i.e. 13 graphitic layers and 40 Å wide for 1500°C H.T.T. versus 20 layers thick by 70 Å wide for 2600°C H.T.T. material). The ribbons undulate and twist along the fiber axis and the degree of alignment varies with graphitization temperature such that the type A fiber has graphitic basal planes, edges and corners comprising the fiber surface while the more graphitic type HM fiber has a surface composed mostly of graphitic basal planes. Detailed discussions of graphite fiber morphology are available in the literature [5].

The fibers studied here were supplied untreated (U) and surface treated (S) by

the manufacturer with his proprietary process to promote matrix adhesion¹. The set of four fibers (AU, AS, HMU and HMS) served as a basis for this study and provided representatives of practical extremes in physical properties and surface treatments.

2.2. XPS measurements

The XPS studies of these fibers were performed using a Physical Electronics Industries model 15-255G double-pass cylindrical mirror analyzer (CMA). The analyzer was used in the retarding mode with pass energies corresponding to a spectrometer resolution (fwhm) of 1, 2 or 4 eV. Initial studies on the fibers "as received" were performed using a Mg X-ray anode; this was replaced by an aluminum anode before the effects of the vacuum heat treatment of the fibers were studied, and so the initial studies were repeated with the new anode.

Samples for the XPS studies were prepared by cutting a large number of fibers to a length of about 10 mm, being careful to avoid handling contamination, and placing them in a nickel holder approximately 10 × 5 × 1 mm. The fibers were then held by a nickel mask which fit tightly into the holder over the fiber ends. The holder was then fastened to a standard sample carousel.

The vacuum chamber was pumped down without baking to a pressure of 1×10^{-9} Pa before taking the spectra.

2.3. Polar/dispersive surface free energy analysis

Surface energetic analyses of the graphite fibers used in this study were determined by measuring the contact angle of a variety of liquids having known polar and dispersive components of their total surface free energy and analyzing the results according to the method proposed by Kaelble [4].

The method assumes additivity between London dispersion γ^D and Keesom polar γ^P interactions between liquids and solids resulting in the total surface free energy γ^T being equal to the sum of the polar and dispersive components

$$\gamma_L^T = \gamma_L^P + \gamma_L^D, \quad (1)$$

$$\gamma_S^T = \gamma_S^P + \gamma_S^D. \quad (2)$$

The assumption holds for low energy solids like polymers where the surface free energy under ambient atmospheric conditions is practically the same as under vacuum. It is assumed that this holds true for graphite fibers also since they are more similar to polymer surfaces than the high energy surfaces where this assumption is not valid.

¹ Hercules Inc., Wilmington, Delaware.

The work of adhesion W_A defined by

$$W_A = \gamma_L (1 + \cos \theta) \quad (3)$$

is introduced and by substitution the relationship between W_A and the polar and dispersive components of the solid of interest is obtained

$$W_A = 2(\gamma_S^{p1/2} \gamma_L^{p1/2} + \gamma_S^{D1/2} \gamma_L^{D1/2}) \quad (4)$$

which rearranges to

$$[\gamma_L (1 + \cos \theta)]^2 / (2\gamma_L^{D1/2}) = \gamma_S^{D1/2} + \gamma_S^{p1/2} (\gamma_L^p / \gamma_L^D)^{1/2}, \quad (5)$$

where γ_L , γ_L^p , γ_L^D are known for the liquids used to contact the surface of interest (table 1) and θ , the contact angle is measured. A plot of $\gamma_L (1 + \cos \theta) / 2\gamma_L^{D1/2}$ versus $(\gamma_L^p / \gamma_L^D)^{1/2}$ will yield a straight line with the slope and intercept providing a solution to γ_S^p and γ_S^D for the surface of interest.

Since the fibers used in this study had a diameter of 8 to 10 μ , optical determination of the contact angle was not feasible. Instead, gravimetric determination of the contact angle was made using a microbalance. Fig. 1 shows the experimental apparatus which has been used before [6,7].

A single fiber carefully cut and handled to avoid damage or contamination was mounted to the end of a small nickel wire hook with a cyanoacrylate adhesive. (Scanning Auger microprobe analysis of this configuration showed no migration of the adhesive to the area where the contact angle was measured.) The fiber/hook was then suspended on the arm of a Cahn RG microbalance. A container of the liquid to be used for the contact angle measurements was slowly raised to the fiber tip. At contact the microbalance would detect a change in force due to the wetting of the

Table 1
Surface free energy components of reference liquids used for contact angle determinations

Liquid	γ_L^T (mJ/m ²)	γ_L^D (mJ/m ²)	γ_L^p (mJ/m ²)
water	72.8	21.8	51.0
glycerol	64.0	34.0	30.0
ethylene glycol	48.3	29.3	19.0
polypropylene glycol PG-1200	31.3	24.5	6.8
formamide	58.3	32.3	26.0
n-hexadecane	27.6	27.6	0
methylene iodide	50.8	48.4	2.4
bromonaphthalene	44.6	44.6	0

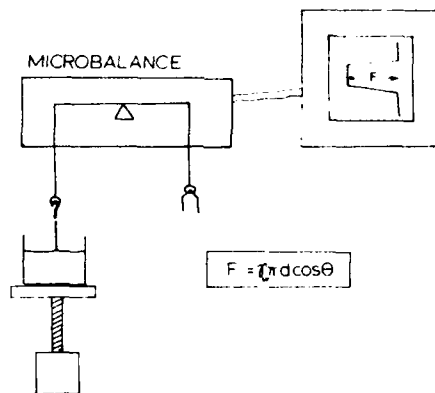


Fig. 1. Schematic diagram of the micro-Wilhelmy technique for measuring contact angles on fibers.

fiber by the liquid. The liquid was raised an additional 0.5 mm to avoid having fiber end effects on the measurements. This force was recorded. Between five and ten fibers were measured for each liquid.

The measured force could then be related to the contact angle through use of equation:

$$F = \gamma_L \pi d \cos \theta, \quad (6)$$

where γ is the surface free energy of the contacting liquid, d is the diameter of circular cross section fibers and θ is the contact angle. d , the fiber diameter was determined for each fiber with a Vickers image splitting eyepiece at 430X after the wetting experiments were conducted. Only one liquid was contacted with each fiber to preclude cross contamination or artifactual changes in fiber surface chemistry. γ_L , the surface free energy for all the liquids used was checked in the laboratory and the liquids were stored in sealed dispenser bottles in the same constant temperature and humidity environment ($22^\circ\text{C} \pm 1/2^\circ$, $30\% \text{ rh} \pm 1\%$) used for the wetting measurements. Since F , γ_L , and d can be evaluated independently, $\cos \theta$ can be evaluated from eq. (6).

3. Results and discussion

3.1. XPS of type A fibers

X-ray photoelectron spectroscopy (XPS) measurements showed that the surface compositions of type A fibers were quite different before and after surface treat-

ment. Typical photoelectron spectra over a kinetic energy range from 100 eV to 1100 eV are shown in fig. 2. Clearly the surface concentrations of oxygen and nitrogen are higher on the AS fibers, fig. 2b, than on the AU fibers, fig. 2a. The larger oxygen concentration on the AS fibers is not unexpected as these fibers have been surface treated with an oxidation technique. The source of the nitrogen is not known precisely but its presence could indicate that the fibers were oxidized in nitric acid. The surface sodium concentration is unexpectedly high and is probably due to residual impurities left in the PAN precursor after spinning.

The carbon, sodium, oxygen and nitrogen 1s photoelectron peak energies and full widths at half maximum (fwhm) were measured at a spectrometer resolution of

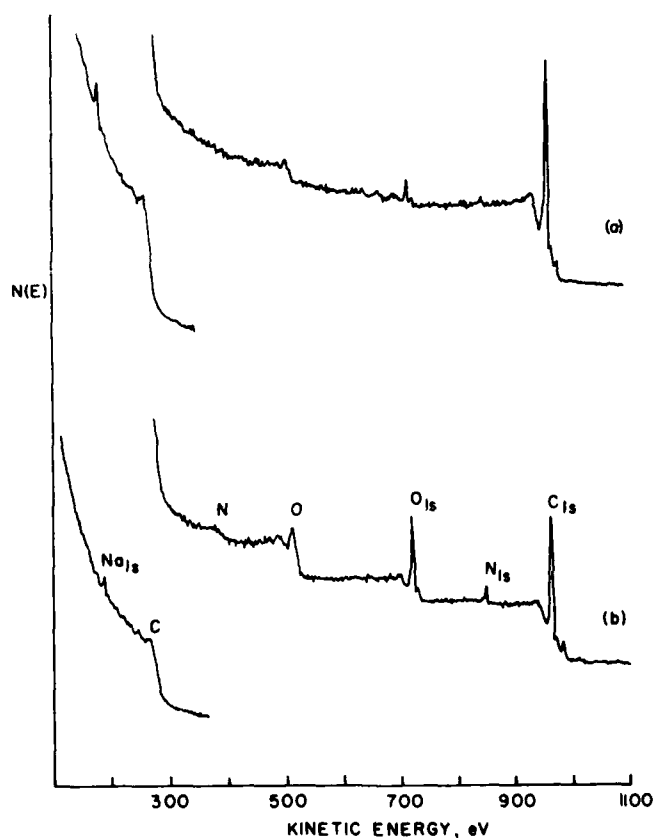


Fig. 2. XPS spectra of type A fibers (a) in the untreated condition (AU) and (b) after surface treatment (AS). Spectrometer resolution was 4 eV.

2 eV. The carbon, oxygen and sodium peak energies agreed within 1 eV for the four sets of fibers studied.

Calculations have been made of the surface concentrations of oxygen, nitrogen and sodium from the XPS data. Cross sections were taken from the data of Scofield [8]. A semi-quantitative comparison of fiber surface composition was made by measuring the peak area above background, correcting for elemental sensitivities and normalizing. The results are shown in table 2.

The oxygen content on the A fiber in the "as received" condition increases with surface treatment by a factor of two. The nitrogen content likewise increases from 2 to 7%. Small ($\approx 3\%$) but significant amounts of sodium are present on the fiber surface.

Nitrogen is almost always present on PAN based graphite fibers that have been graphitized at low temperature. Sources of nitrogen could be residual material from ineffective graphitization, residual impurities left in the fiber from the spinning operation (e.g. NaSCN) or the result of surface treatment. The nitrogen peaks observed here on both the AU and AS fibers were within 0.4 eV and had a binding energy of

Table 2
Elemental composition of graphite fiber surfaces determined by integration of XPS peaks

Fibers	C	O	Na	N	S
"as received"					
AU	86	9	3	2	
AS	70	20	4	7	
300°C V.T.					
AU	79	14	6		2
AS	72	18	6	3	
600°C V.T.					
AS	84	7	5	3	1
750°C V.T. + H₂					
AS	94	3	1	1	1
"as received"					
HMU	95	5			
HMS	89	9			
300°C V.T.					
HMU	96	4			
HMS	97	3			

about 400 eV. This suggests no change in type of nitrogen with surface treatment. Also the value of 400 eV corresponds to C-N or to C-NH₂ type linkages [15]. This is very similar to the nitrogen photoline detected by Barber et al. [2]. Recently, Thomas and Walker [3] have also described nitrogen on the surface of AS graphite fibers but have attributed the spectra as characteristic of C-O-N type linkages but neither binding energies or spectra were given in the publication. Hopfgarten [1] has detected nitrogen with XPS on similar graphite fibers at 400 eV but did not speculate on its source.

The distribution of the sodium within the sampling depth of the spectrometer for these fibers was determined by comparing the Na 2s to Na 1s photoelectron ratio. The 2s photoelectrons have a kinetic energy of 1190 eV versus 180 eV for the 1s photoelectrons and therefore an escape depth two and one-half times greater. The sodium 1s to 2s ratios are 4.2 and 3.7 for the AU fibers and 2.0 and 1.8 for the AS fibers. This indicates a higher surface concentration of sodium on the AU fiber even though the total amount detected is the same for both fibers.

The source of sodium is believed to be residual sodium-sulphur salts used as a coagulant in the PAN spinning process. Hopfgarten [1] has also seen these species on some PAN based graphite fibers and attributes the sodium to residual sodium thiocyanate used in the PAN polymerization. Definitive energy assignments were not possible here because of the low signal to noise ratio attainable. Bulk X-ray analysis has shown levels of sodium for these fibers of 1–2000 ppm [9]. Although bulk concentrations of this level would not be expected to give appreciable surface concentrations, evidence of these compounds and their tendency to migrate under time-temperature conditions is provided in the literature [10].

An attempt was made to distinguish between physisorbed oxygen containing species by vacuum treatment for 12 h at 300°C. This treatment was not conducted in the XPS spectrometer system and involved air and moisture exposure prior to XPS analysis. The oxygen concentration for the AS fiber remained about the same but the sodium content increased (3–6%) and the nitrogen content decreases (7–3%). The oxygen content on the AU fiber increased with this treatment, however leading to suspicions that the air and moisture exposure after 300°C vacuum treatment may have oxidized a greater portion of this fiber surface. Support for this mechanism can be seen in fig. 3. The O 1s peak after 300°C V.T. (curve a) shows an additional shoulder at ≈ 950 eV not present in the "as received" state (curve b).

The stability of the surface species was investigated by treating the fibers with high temperature vacuum exposure. One sample of AS fiber was treated in vacuum of $< 10^{-7}$ Torr at 600°C for 1 h. Another sample was treated on vacuum of $< 10^{-7}$ Torr at 750°C for 1 h followed by exposure to hydrogen at 750°C. In this treatment the amount of hydrogen added to the gas phase in contact with the fiber at 750°C was the equivalent of one monolayer based on sample size and surface area. The reaction products resulting from this exposure as determined by mass spectrometric analysis contained significant amounts of H₂S [11].

XPS analysis of the AS fiber after both of these treatments was determined and

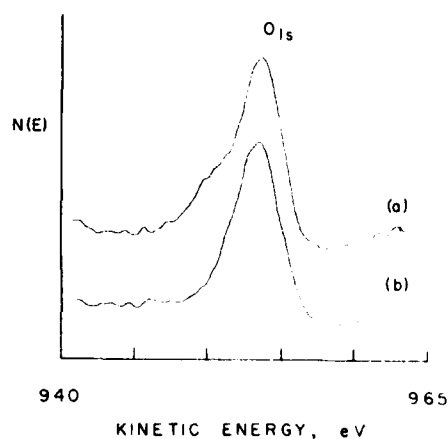


Fig. 3. Oxygen 1s spectra of AS fiber (a) after 300°C V.T. and (b) in the "as received" state.

the results tabulated in table 2. The 600°C V.T. removed over half of the surface oxygen groups but did not appreciably affect the intensity of N or S photolines. Treatment at 750°C followed by hydrogen reduction did, however, greatly reduce all of the surface species. The oxygen level was reduced to about three percent and the sodium, nitrogen and sulphur were reduced to the one percent level.

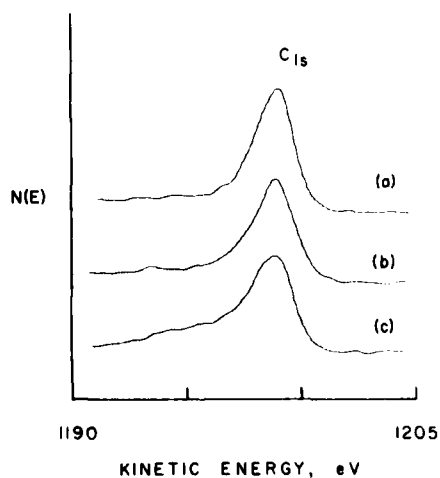


Fig. 4. Carbon 1s spectra of AS fiber (a) after 750°C and hydrogen treatment (b) after 600°C vacuum treatment and (c) in the "as received" state.

High resolution C 1s spectra show that the removal of oxygen species with treatment is paralleled by a narrowing of the C 1s peak (fig. 4) indicating a more graphitic type of carbon [12].

3.2. XPS of HM fibers

Broad scan XPS spectra for the type HMU fibers and HMS fibers in the "as received" state are shown in fig. 5. These spectra are quite different than the spectra from the A fibers (fig. 2). Oxygen is the only surface species detected other than carbon on these surfaces. The surface treated HMS fiber has more oxygen than the

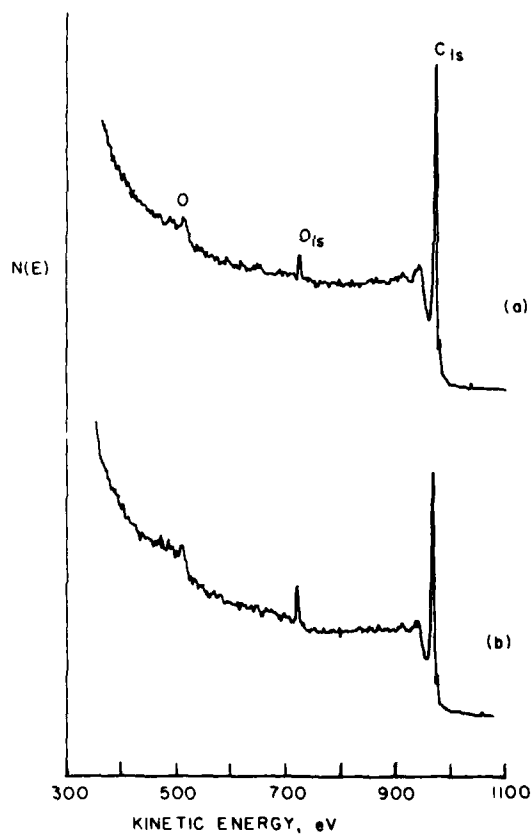


Fig. 5. XPS spectra of type HM fibers (a) in the untreated condition (HMU) and (b) after surface treatment (HMS). Spectrometer resolution was 4 eV.

untreated fiber (9% versus 5%) as shown in table 2. Nitrogen, sodium and sulphur are not present probably due to the much higher graphitization temperature given this fiber (i.e. $\approx 2600^\circ\text{C}$) even though the PAN precursor polymer was the same.

The carbon and oxygen 1s photoelectron peak energies and full widths at half maximum were also measured at a spectrometer resolution of 1 eV. The carbon and oxygen peak energies from the different fibers were within 0.2 eV for carbon and 0.5 eV for oxygen. The fwhm for carbon and oxygen were measured to be 1.6 eV and 3.4 eV respectively. The fwhm for oxygen is similar to that from the AS and AU fibers, but the fwhm for carbon is considerably narrower than that from the AS and AU fibers (1.6 eV compared to 2.25 eV), fig. 6. This result is not unreasonable as the higher graphitization temperature for the HMS and HMU fibers should result in more truly graphitic surfaces.

The surface concentration of oxygen determined on the HM fibers in the "as received" state (table 2) shows that the surface treatment doubles the oxygen concen-

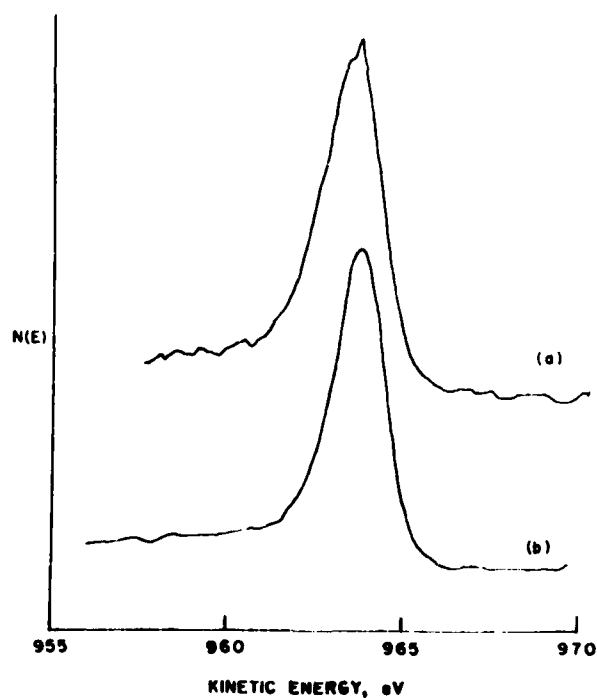


Fig. 6. Carbon 1s spectra for (a) type AS fibers and (b) type HMU fibers. Spectrometer resolution was 1 eV.

Table 3
Contact angles for graphite fiber surfaces

Liquid	AU		AS		HMU		HMS	
	as rec'd	300°C V.T.	as rec'd	300°C C.T.	as rec'd	300°C V.T.	as rec'd	300°C V.T.
water	41° ± 4°	44° ± 4°	29° ± 4°	33° ± 4°	75° ± 5°	79° ± 2°	46° ± 8°	68° ± 4°
glycerol	33° ± 2°	40° ± 1°	25° ± 1°	42° ± 9°	46° ± 3°	50° ± 5°	44° ± 7°	43° ± 3°
ethylene glycol	35° ± 6°	30° ± 6°	31° ± 7°	29° ± 2°	40° ± 4°	36° ± 6°	32° ± 8°	32° ± 1°
polypropylene	3° ± 3°	25° ± 1°	3° ± 3°	25° ± 1°	3° ± 3°	25° ± 4°	3° ± 3°	28° ± 3°
glycol PG1200	37° ± 1°	24° ± 7°	22° ± 5°	27° ± 3°	50° ± 6°	47° ± 2°	37° ± 4°	34° ± 5°
formamide	18° ± 8°	27° ± 7°	22° ± 7°	23° ± 7°	0°	23° ± 7°	0°	23° ± 7°
n-hexadecane	23° ± 5°	41° ± 11°	23° ± 5°	30° ± 12°	45° ± 2°	41° ± 2°	28° ± 8°	41° ± 4°
methylene iodide	29° ± 3°	20° ± 4°	26° ± 3°	21° ± 3°	29° ± 3°	30° ± 3°	30° ± 3°	27° ± 3°
bromonaphthalene								

tration. Treatment at 300°C in vacuum reduces the surface oxygen content on both fibers. Previous work [13] has shown the evolution of carbon monoxide, carbon dioxide and water from these surfaces at temperatures well below 300°C. Likewise estimation of surface energetic heterogeneities from krypton adsorption isotherms indicates the same level of surface heterogeneity as oxygen content determined by XPS (i.e. 1–4%, versus 3–4%), see ref. [13].

3.3. Polar/dispersive free energy analysis

The results of gravimetric determinations of contact angles on these graphite fibers are listed in table 3. The value of θ listed is calculated from eq. (6) and is the average for all determinations on each type of fiber with the indicated liquid. In general, the contact angle increases with increasing surface tension of the contacting liquid and decreases with surface treatment for each fiber type.

Plots were made according to eq. (5). Some typical plots are shown in fig. 7. A best fit straight line is determined for each data set using linear regression analysis and the slope and intercept are used to determine the γ_S^P , γ_S^D , and γ_S^T for each fiber and treatment. The results are shown in table 4.

Comparing values of the total surface free energy γ_S^T for the fibers and surface treatments studied leads to trends similar to those observed with the XPS surface analysis. That is, surface treatments increase the total surface free energy γ_S^T over the same fiber that has been untreated for both the A and HM fibers.

Inspection of the polar (γ_S^P) and dispersive (γ_S^D) components of the surface free energy indicates that the dispersive portion remains unchanged with treatment and that all of the change in γ^T is due to a change in γ^P the polar component. This was observed by Kaelble [4] for three similar fibers.

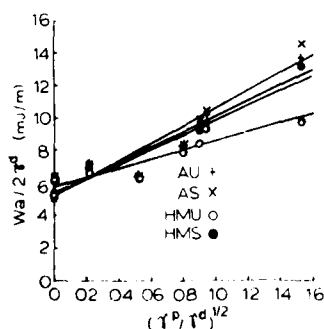


Fig. 7. Typical plots of $W_A/2\gamma^D^{1/2}$ versus $(\gamma^P/\gamma^D)^{1/2}$ for AU, AS, HMU and HMS fibers in the "as received" states and the "best" linear regression analysis line through those points.

Table 4
Polar, dispersive and total surface free energy of graphite fiber surfaces

Fibers	Surface free energy		
	γ_S^P (mJ/m ²)	γ_S^D (mJ/m ²)	γ_S^T (mJ/m ²)
"as received"			
AU	23.6 ± 2.6	27.4 ± 0.3	51.0 ± 2.6
AS	30.0 ± 1.7	26.4 ± 0.1	56.4 ± 1.7
300°C V.T.			
AU	24.1 ± 1.4	26.3 ± 1.1	50.4 ± 1.4
AS	26.8 ± 1.4	26.0 ± 1.2	52.8 ± 1.4
750°C V.T. + H ₂			
AS	12.3 ± 1.5	32.3 ± 1.5	44.6 ± 1.5
"as received"			
HMU	8.1 ± 3.0	33.0 ± 1.2	41.1 ± 3.0
HMS	20.7 ± 4.0	28.2 ± 0.3	48.9 ± 4.0
300°C V.T.			
HMU	7.4 ± 0.9	32.0 ± 0.9	39.4 ± 0.9
HMS	12.8 ± 1.7	30.2 ± 0.4	43.0 ± 1.7

3.4. Relationship between XPS and surface energetics

Surface treatments that increase the surface oxygen content as determined by XPS also increase the polarity of the surface as detected by contact angle measurements. Specifically, for the A fiber in the "as received" state, the XPS oxygen content increased from 9% to 20% with surface treatment and surface energetic analysis indicates an increase in γ_S^P of from 24 to 30 mJ/m² for the same fibers. XPS of the HM "as received" fiber showed an oxygen increase of 5% to 9% with surface treatment and surface energetic analysis indicates an increase in γ_S^P of from 8 to 21 mJ/m².

The lack of proportionality between increases in polarity with increases in surface species is not unexpected if one takes into account the nature of the fiber surface and the type of measurements conducted. The corners and edges of graphitic crystallites are sites for oxidative attack [14]. Although the crystallite size increases with graphitization temperature (i.e. 70 Å versus 40 Å) there are less exposed corners and edges on the HM fiber because of the better circular alignment. Therefore, a small increase in surface oxygen would be dispersed over a large area of the fiber

surface and would be expected to have a large effect. Whereas on the A fibers additional oxygen species might be located near the species already present and consequently their effect per additional atom on a macroscopic measurement like contact angles would decrease with increasing surface population.

The 300°C V.T. surface energetic results also conform to results obtained by XPS. The γ_S^P for AS is slightly greater than for AU treated similarly but in both cases less than either fiber in the "as received" state. The HMU and HMS values of γ_S^P are reduced after 300°C V.T. also. The AS fiber treated at 750°C with hydrogen displays a large decrease (30 to 12 mJ/m²) with a reduction in surface oxygen of 20% to 3%.

The relationship between the polar component of the surface free energy γ_S^P and the surface composition is represented graphically in fig. 8. Here the polar component of the surface free energy is plotted as ordinate versus atomic percent surface oxygen as measured by XPS as abscissa. Points on the graph are for the fiber surfaces measured based on the data in tables 2 and 4. The vertical and horizontal bars on each point represent the estimated error associated with each measurement.

It is obvious from the data that there is a definite relationship between the polar component of the surface free energy and XPS measured surface oxygen content. A higher γ_S^P is associated with a larger percent oxygen. (The complicating effects of molecular states of each species i.e. nitrogen-carbon complexes, sodium-oxygen species, etc., cannot be evaluated at this time because of the instrumental limitations.) However, attempts at determining γ_S^P as a function of surface sites would have an effect only on the AS and AU points (as received and 300°C V.T.) and would be

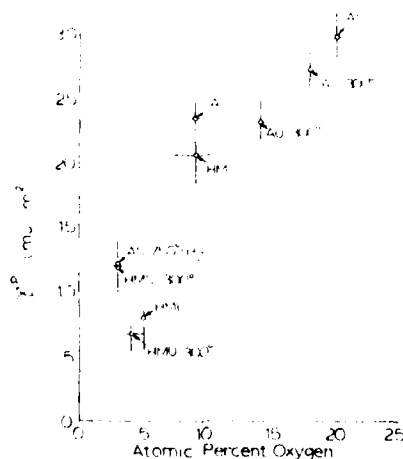


Fig. 8. Plot of the polar component of graphite fiber surface free energy (γ_S^P) versus XPS determined oxygen content for all graphite fibers and treatments studied.

expected to shift them toward the ordinate but would not be expected to alter the general observed correspondence between these two parameters.

It is also obvious that a measurement obtained in high vacuum (XPS) is relatable to an air determined measurement (γ_S^P). This attests to the efficiency of species added during surface treatment for promoting adhesion even though these surfaces are exposed to be ambient air environment before fabrication into a composite.

4. Conclusions

Surface treatments of graphite fibers which promote better fiber matrix adhesion result primarily in an increase in surface oxygen concentration as measured by XPS and an increase in the total surface free energy of the graphite fiber surface as determined by contact angle measurement. The change in the total surface free energy comes about primarily through an increase in the polar component of the fiber surface free energy. Consequently fiber surface treatments which oxygenate the surface are effective in promoting increased adhesion by increasing surface polarity as well as by increasing the surface concentration of oxygen.

The added surface groups retain their polar character after exposure to the environment. A definite relationship between vacuum measured surface groups and air measured macro contact angles exists for all of the fibers and surface treatments measured.

References

- [1] F. Hopfgarten, *Fibre Sci. Technol.* 11 (1978) 67.
- [2] M. Barber, P. Swift, F.L. Evans and J.M. Thomas, *Nature* 227 (1970) 1131.
- [3] C.R. Thomas and I.J. Walker, *Proc. 5th London Intern. Carbon and Graphite Conf.* (Sept., 1978) p. 520.
- [4] D.H. Kaelble, P.J. Dynes and F.H. Cirlin, *J. Adhesion* 6 (1974) 23.
- [5] R.J. Diefendorf and E.W. Tokarsky, *The Relationship of Structure to Properties in Graphite Fibers*, AFML-TR-72-133 (1971).
- [6] G. Mozzo and R. Chabard, *Society of the Plastic Industry, Inc., 23rd Annual Tech. Conf. Section 9-C* (1968) p. 1-8.
- [7] R.L. Bendure, *J. Coll. Int. Sci.* 42 (1973) 137.
- [8] J.H. Scofield, *J. Electron Spectry. Relat. Phenom.* 8 (1976) 129.
- [9] L.T. Drzal, *Carbon* 15 (1977) 129.
- [10] D.W. Gibson, U.S. Patent No. 3, 413, 094 (26 Nov., 1968).
- [11] D.L. Hall, *Development of Surface Interactions at the Polymer-Metal Interface*, AFML-TR-79-4100 (Aug., 1979).
- [12] R.L. Willis, B. Titton and D.K. Skinner, *J. Appl. Phys.* 43 (1972) 4412.
- [13] L.T. Drzal, J.A. Mescher and D.L. Hall, *Carbon* 17 (1979) 375.
- [14] N.R. Laine, F.J. Vastola and P.J. Walker, Jr., *J. Phys. Chem.* 67 (1963) 2030.
- [15] T.A. Carlson, *Photoelectron and Auger Spectroscopy* (Plenum Press, New York, 1975) p. 352.

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